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Novel direct amination of glycerol over heteropolyacid-based catalysts†

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The direct amination of glycerol with dimethylamine (DMA) was studied over catalysts based on salts of phosphomolybdic acid. The highest yield of (dimethylamino)acetone (33%) was observed over a catalyst containing 50 wt% of $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ supported on a mesoporous silica. The corresponding sample showed good dispersion of the active phase leading to an increased number of available acid sites. With respect to the observed products, a reaction scheme was established explaining notably that the formation of 1,3-bis-dimethylamine-2-propanol and (dimethylamino)propanol was not possible due to the blocking of the required strong acid sites by DMA under reaction conditions.

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Introduction

Amines are important products in organic synthesis.^{1,2} They are used in numerous applications such as pharmaceuticals, crop protection (pesticides and insecticides), food processing, solvents for paints, fuel additives, or for oil & gas treatment.³

Amines can be obtained by amination of olefins, ketones and alcohols. In the latter case, two main processes are well established: reductive amination (often including the borrowing hydrogen mechanism) and direct amination (Scheme 1). Reductive amination processes involve the reaction of an alcohol with ammonia or alkylamines on metal catalysts, typically nickel or cobalt supported on silica or alumina. Depending on the substrate and the product, the temperature of this reaction ranges from 150 to 210 °C under a hydrogen pressure between 17 and 20 bar.⁴ Two well-known examples of reductive amination are i) the synthesis of triethylamine from ammonia and ethanol over a Co/SiO₂ catalyst at 200 °C and a pressure of 200 bar and ii) the synthesis of fatty amines from long chain fatty alcohols with DMA over Cu/Ni catalysts at 210 °C and a pressure between 50 and 200 bar.⁵⁻⁷ On the other hand, the direct amination uses solid acid catalysts and proceeds at low pressure, in a typical temperature range between 250 and 290 °C. Hereby, most of the research efforts have been focused on the use of shapeselective catalysts, *e.g.*, zeolites. Zeolites are frequently used for the synthesis of small chain aliphatic diamines,⁸ or cyclic amines⁹ from the corresponding amino alcohols. Y-zeolites, ZSM-5 and mordenites in their protonated form are the most often employed molecular sieves.¹⁰ The main advantage of direct amination notably relies on the use of such low cost catalysts compared to the metal catalysts employed in the reductive amination.

Recently, the use of polyols has drawn specific attention, due to the demand in diamines and polyamines, especially ethylenediamine and its polymers.¹¹ One industrially interesting polyol is glycerol, which is widely available, since it is a co-product from the transesterification of vegetable oils for biodiesel production. Hence, valorization of glycerol has become a key issue in order to balance the overall economic viability of the biodiesel industry, with many possible targets (*i.e.*, chlorination to epichlorohydrin, oxidation to fine chemicals, dehydration to acrolein, *etc.*).^{12–18}

In the present paper, we report on the direct amination of glycerol with dimethylamine over heteropolyacid-based catalysts with 3-(dimethylamino)-propane-1,2-diol (DMAPA) and dimethylamino-2-propanone (DMA-acetone) as targets, the



Scheme 1 Amination reaction of alcohols: reductive pathway (up) and direct pathway (down).

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former being used in the food industry, botanical extracts, oil & gas treatment, and pharmaceutical and personal care applications, and the latter in solvents, feed additives, in the agrochemical industry, *etc.* Heteropolyacids (HPAs) are environmentally friendly and economically viable Brønsted acids.^{19–22} They are widely studied in the field of catalysis and notably for the valorization of biomass.²³ Hereby, HPAs offer a unique feature to enabling fine modification of their acidity – and thereby of their catalytic properties – *via* the tuning of their composition, namely, by varying the central atom, the addenda atoms and the counter ions.^{24–26}

Phosphomolybdic acid was neutralized to different extents with cesium to modulate its acidic properties. It was characterized, tested, and optimized in the reaction of direct amination of glycerol using a Design of Experiment (DoE)driven strategy.

Experimental

Catalyst preparation

Phosphomolybdic acid ($H_3PMo_{12}O_{40}$) is commercially available as crystalline hydrate (Sigma Aldrich, >99%). Neutralized salts of phosphomolybdic acid ($Cs_3PMo_{12}O_{40}$ and $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$) were prepared by a precipitation method. An aqueous solution of Cs_2CO_3 (0.1 M, Fluka) was added *via* a liquid pump into an aqueous solution of $H_3PMo_{12}O_{40}$ (0.1 M). The temperature of the mixture was maintained at 45 °C under vigorous stirring. After 2 h, the solid was recovered by removing the solvent under reduced pressure. The sample was then dried at 70 °C for 24 h.

The preparation of Cs_{2.5}H_{0.5}PMo₁₂O₄₀ supported on silica was carried out in two steps. First, the silica carrier was impregnated with cesium carbonate. 2.5 g of silica support (CARIACT Q-10, kindly provided by Fuji Silysia) and 30 mL of ethanol were stirred at 60 °C. Then, the desired amount of cesium carbonate (0.1 M, Fluka) was added. After 30 minutes, the solvent was evaporated, and the solid was dried at 60 °C for 2 h. The as-prepared silica was then impregnated with commercial phosphomolybdic acid; the support suspended in 30 mL of extra-dry ethanol. The required amount of HPA dissolved in a minimum quantity of ethanol was subsequently added. After 30 min, the solvent was evaporated under vacuum at 60 °C, and the obtained solid was dried at 50 °C for two hours. Catalysts supported on silica with nominal loadings of 30, 50 and 70 wt% of Cs_{2.5}H_{0.5}PMo₁₂O₄₀ were prepared, and the corresponding samples were labeled 30CsPMo, 50CsPMo and 70CsPMo, respectively.

Catalyst characterization

The textural properties were determined from N_2 adsorptiondesorption isotherms recorded at the liquid nitrogen temperature using an ASAP 2010 Micromeritics apparatus after outgassing the solids at 130 °C for 2 h. The specific surface area, the pore volume, and the pore size distribution were obtained by using the BET and BJH methods, respectively. The acid properties of the catalysts were determined by temperature-programmed desorption of NH_3 (NH_3 -TPD). A typical NH_3 -TPD test was carried out as follows: 250 mg of catalyst was pretreated in a He flow (30 mL min⁻¹) at 250 °C for 2 h in order to remove the physisorbed and crystal water. Then, the sample was cooled to 130 °C, and NH_3 pulsed injections were carried out until saturation. The TPD profiles were monitored using a TCD (Thermal Conductivity Detector) and a mass spectrometer as detectors, and recorded from 130 to 600 °C at a 10 °C min⁻¹ heating rate.

Raman spectra were recorded on a Jobin-Yvon LabRam Infinity apparatus equipped with a CCD (Charge Coupled Device) detector operating at the liquid nitrogen temperature. A D2 filter was used to protect the catalyst structure from thermal degradation by the laser beam heat ($\lambda = 532$ nm). The spectra were recorded in the range between 200 and 1400 cm⁻¹. The homogeneity of the samples was checked by performing the analysis on at least three different particles for each sample.

Elemental analysis was performed by X-ray fluorescence energy dispersive X-ray spectroscopy (EDS) on a Hitachi S3600N electron microscope equipped with a Thermo Ultradry EDS detector using an acceleration voltage of 25 kV.

Catalytic test

The direct amination of glycerol was carried out in a fixed bed down-flow reactor (110 mm height and 8 mm internal diameter) with a catalyst bed (1 g of catalyst) set at the middle of the reactor, in the isothermal zone. The catalyst was loaded between two layers of SiC with a particle size of 0.1 mm. The temperature was controlled by a thermocouple located near the catalyst bed. Nitrogen was used as a carrier gas at a flow rate of 30 mL min⁻¹, which was controlled by a mass flow controller (Brooks). Glycerol and dimethylamine (DMA) aqueous solutions (40 wt% each) were fed via two HPLC pumps (Gilson) with flow rates of 0.1 mL min⁻¹ and 2.4 mL min⁻¹, respectively, and evaporated upfront the reactor at 230 °C. The glycerol: DMA: N2: H2O molar ratio was 6.1%:6.4%:17.2%:70.4%. The reaction temperature was fixed to 290 °C. The reaction products together with unconverted glycerol were collected in two hour intervals in a trap at room temperature and analyzed offline using gas chromatography and high-performance liquid chromatography. GC analyses were performed on an Agilent 6890 GC using a flame ionization detector and equipped with a Zebron CP Sil 5 CB semi-capillary column (30 m length, 3 µm film thickness, 0.53 mm internal diameter). High Performance Liquid Chromatography (HPLC) was used to quantify the amount of glycerol using a refractory index detector (Shodex RI-101) and a Rezex ROA-organic column (Phenomenex, 300 × 7.80 mm). Glycerol conversion and product selectivities were calculated using eqn (1) and (2). The carbon balance was calculated as the percentage of the reacted carbon atoms found in the products relative to the total number of carbon atoms introduced in the reactor (eqn (3)).

GLY conversion (%) =
$$\left(\frac{n_{\rm i} {\rm GLY} - n_{\rm f} {\rm GLY}}{n_{\rm i} {\rm GLY}}\right) \times 100$$
 (1)

Selectivity (%) =
$$\left(\frac{n_{\rm f} \text{ products}}{n_{\rm i} \text{ GLY} - n_{\rm f} \text{ GLY}}\right) \times 100$$
 (2)

Carbon balance(%) =
$$\left(\frac{n_{\rm f} {\rm GLY} + n_{\rm f} {\rm product}}{n_{\rm i} {\rm GLY}}\right) \times 100$$
 (3)

The experimental design was generated by the statistical software Design-Expert, version 5.0.8, Stat-Ease Inc. The response surface methodology was used in order to investigate the influence of the varied parameters (reaction temperature, DMA/GLY molar ratio and total reactant flow) on the response variables.

Results and discussion

Characterization of bulk HPA catalysts

The catalysts were analyzed by NH₃-TPD, nitrogen physisorption, elemental analysis (EDS) and IR-Raman spectroscopy.

The acid properties of the unsupported phosphomolybdic acid salts were determined by NH₃-TPD and the corresponding results are reported in Table 1. As expected, the entirely neutralized cesium salt of phosphomolybdic acid (Cs₃PMo₁₂O₄₀) exhibited no ammonia uptake (0 mmol g⁻¹), meaning that a total neutralization of the acidic protons was achieved. These results are in contradiction to the literature, reporting that stoichiometric salts partially precipitate as a mixture of the parent HPA and cesium salt.^{27,28} Upon partial neutralization with cesium (Cs_{2.5}H_{0.5}PMo₁₂O₄₀), the amount of acid sites increased only slightly to 0.01 mmol g⁻¹. This surprising result could be due to the formation of a layer of entirely neutralized phosphomolybdic acid (Cs₃PMo₁₂O₄₀) on the outer surface of the catalyst.

The textural properties of the bulk HPAs were measured by N_2 adsorption-desorption, and the corresponding results are summarized in Table 1. The stoichiometric Cs salt of phosphomolybdic acid exhibited a specific surface area of

Table 1 Textural properties of the prepared samples								
Catalyst	Specific surface area $(m^2 g^{-1})$	Pore volume $(cm^3 g^{-1})$	Average pore radius (nm)	NH ₃ uptake (mmol g ⁻¹)				
Cs ₃ PMo ₁₂ O ₄₀	126	0.184	41	0				
$Cs_{2.5}H_{0.5}PMo_{12}O_{40}$	131	0.202	47	0.01				
SiO ₂	268	1.21	18					
30CsPMo	234	0.77	12	0.03				
50CsPMo	196	0.54	11.2	0.17				
70CsPMo	212	0.32	12.2	0.06				

126 m² g⁻¹, which is in the same range as the partially neutralized salt ($Cs_{2.5}H_{0.5}PMo_{12}O_{40}$), exhibiting 131 m² g⁻¹. Both samples also exhibited comparable pore volumes (0.184 and 0.202 cm³ g⁻¹, respectively) and average pore radii (41 and 47 nm, respectively).

Characterization of supported HPA catalysts

In the following, the acidity of the silica-supported samples (Cs_{2.5}H_{0.5}PMo₁₂O₄₀, this active phase being selected after the tests on the bulk compounds) was probed by ammonia TPD using a mass spectrometer for the detection of the desorbed ammonia species (Fig. 1). In all the cases, the amount of acid sites increased (Table 1). This increase is definitely not related to the presence of acid sites on the silica support, which is neutral, but is exclusively explained by the enhanced dispersion of the HPA on the support. While the unsupported Cs_{2.5}H_{0.5}PMo₁₂O₄₀ exhibited a total ammonia uptake of 0.01 mmol g^{-1} (Table 1), the supported samples, namely 30CsPMo, 50CsPMo and 70CsPMo, showed 0.03, 0.17 and 0.06 mmol g^{-1} , respectively. The shape of the desorption profile (Fig. 1) further shows that the samples mainly exhibit weak acid sites (desorption temperature < 300 °C; Fig. 1).²⁹ The fact that only weak sites were observed can be ascribed to electronic interactions between the HPA and the support, as described in the literature, which, while stabilizing the HPA, decrease their acid strength.^{23,30,31}

For the supported catalysts, the mesoporous silica (CARiACT Q-10, Fuji Silysia) was chosen as a carrier in order to avoid internal diffusion limitations. Correspondingly, the impregnated catalysts show a type IV isotherm, with a hysteresis characteristic of mesoporous samples (Fig. S1†). Upon impregnation of the support with the active phase, the specific surface area decreased from 268 m² g⁻¹ (bare support) to 234, 196 and 212 m² g⁻¹ for the catalysts containing 30, 50 and 70 wt% of the active phase, respectively (Table 1). In all the cases, the decrease is rather limited to a small extent due to the fact that the active phase ($Cs_{2.5}H_{0.5}PMO_{12}O_{40}$) itself exhibits porous properties (*cf.* Table 1, line 2). On the other hand, the average pore diameter of the support was



Fig. 1 NH₃-TPD profile of 30CsPMo (a), 50CsPMo (b) and 70CsPMo (c).

Table 2	Quantitative EDS and XRF	analyses of	f supported salts of	phosphomolybdic acid
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	Atom%											
Catalyst	O (EDS)	O (XRF)	O theor.	Si (EDX)	Si (XRF)	Si theor.	Mo (EDS)	Mo (XRF)	Mo theor.	Cs (EDS)	Cs (XRF)	Cs theor.
30CsPMo	63.8	67.7	67.7	30.3	26.0	28.6	4.9	4.7	3.1	0.93	1.0	0.65
50CsPMo	59.5	68.9	68.5	22.6	17.5	24.0	14.1	10.2	6.1	3.7	2.1	1.3
70CsPMo	73.1	69.8	$69.9(73.3)^a$	1.8	11.3	$17.5(0)^{a}$	20.9	14.2	$10.4(22)^a$	4.9	3.0	$2.1 (4.6)^a$
^a Theoreti	cal amoun	t for pure	Cs _{2.5} H _{0.5} PMo ₁	$_{2}O_{40}$.								

significantly affected upon impregnation and decreased from 18 nm to 11–12 nm for the CsPMo-containing samples. Further, note that the pore size distribution is rather fine for all the samples, indicating a uniform covering of the pores, except when too large amounts of the active phase were used (70 wt%; Fig. 2).

Elemental analysis (EDS and XRF) was carried out on the supported catalysts to check their elemental composition and dispersion (Table 2 and Fig. S2[†]). In the case of 30CsPMo, the as-determined composition by XRF and EDS was very close to the theoretical one. On the other hand, for the 50CsPMo and 70CsPMo samples, the detected amount of Mo and Cs by EDS was significantly higher than the theoretical ones. This trend was less pronounced for the elemental composition determined by XRF analysis over these two samples. In fact, the elemental composition determined by EDS for the 70CsHPA/SiO₂ sample corresponded to the one of pure Cs_{2.5}H_{0.5}PMo₁₂O₄₀. This can be explained by the low analysis depth of EDS (100 nm). Indeed, a theoretical calculation shows that only 62% of the surface is covered by the HPA salt when using 30 wt% of the active phase (Scheme 2).³² On the other hand, when increasing the amount of the active phase, the coverage increases to 146% and 340% for 50 wt% and 70 wt% of the active phase, respectively, which corresponds to the formation of a multilayered structure. In that case, EDS will obviously give the elemental composition of bare CsPMo, which is indeed the case (Table 2, line 3).



Fig. 2 Pore size distribution for bare silica (+), 30CsPMo(x), 50CsPMo(o) and $70CsPMo(\Box)$.

In the following, we checked if the structure of the active phase was preserved after impregnation on silica. Thus, IR-Raman spectroscopy (Fig. 3) was used in order to verify the presence of the heteropolyacid compounds. The Raman spectra of the supported catalysts exhibited strong bands assigned to the following vibrations: $v_s(Mo=O)$ at 982 cm⁻¹, $v_s(Mo-Oa)$ at 245 cm⁻¹ and $v_s(Mo-O-Mo)$ at 256 and 237 cm^{-1.33} The low intensity – but characteristic – shoulder at 994 cm⁻¹ was assigned to the formation of MoO₃ particles, thus suggesting a very limited decomposition of the HPA.³⁴ This confirms the preservation of the HPA structure upon supporting on SiO₂.

Nevertheless, it is noteworthy that some particles of the catalyst based on 30CsPMo exhibited no characteristic signal of the HPA compound, thus meaning that the active phase was not homogeneously dispersed on all the catalyst particles, which had significant impact on the catalytic performance. On the other hand, the catalyst based on 70CsPMo contained some particles that consisted of pure HPA. Consequently, only the catalyst based on 50CsPMo exhibited a homogeneous distribution of the active phase.

Catalytic results

The catalytic performance of the solids is reported in Table 3. The stoichiometrically neutralized phosphomolybdic acid – $Cs_3PMo_{12}O_{40}$ – showed a high conversion of glycerol (25%) but a rather low selectivity to DMA-acetone (29%). On the other hand, the partially neutralized salt $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ showed a significantly higher selectivity of 63% but at a lower conversion rate of 8% (Table 3). Since both catalysts exhibit rather comparable specific surface areas of 126 and 131 m² g⁻¹ and acidities of 0 and 0.01 mmol g⁻¹ (Table 1),



Scheme 2 Silica coverage for 30 wt% (a); 50 wt% (b); and 70 wt% of CsHPA (c).

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Fig. 3 Raman spectra of 30CsPMo (a), 50CsPMo (b), and 70CsPMo (c).

Table 3 Catalytic test results

	X	CB	Selectivity (%)	Y	
Catalyst	(%)	(%)	DMA-acetone	DMAPA	(%)
Cs ₃ PMo ₁₂ O ₄₀	25	95	29	0	7
Cs _{2.5} H _{0.5} PMo ₁₂ O ₄₀	8	95	63	0	5
30CsPMo ^a	61	62	2	0	1
50CsPMo ^a	33	85	33	0	11
70CsPMo ^a	8	85	30	0	2

X = conversion; CB = carbon balance; *Y* = (DMA-acetone + DMAPA) yield; reaction conditions: *T* = 290 °C, *P* = 1 bar, glycerol:DMA:N₂: H₂O = 6.1%:6.4%:17.2%:70.4%, contact time = 0.25 s, reaction time = 3 h. ^{*a*} Same conditions but time = 0.36 s.

respectively, no correlation between the activity and the specific surface area or acidity could be found.

In the next step, we decided to study the possibility of supporting Cs_{2.5}H_{0.5}PMo₁₂O₄₀ (CsHPA) to increase the accessibility of the acid sites. The choice for Cs_{2.5}H_{0.5}PMo₁₂O₄₀ as the active phase was motivated by its rather high selectivity to DMA-acetone (63%), but at a low conversion (8%). Consequently, Cs_{2.5}H_{0.5}PMo₁₂O₄₀ was impregnated over a commercial silica (CARiACT Q-10) at the different loadings of 30, 50, and 70 wt%. The catalytic performance of the asobtained supported catalysts is listed in Table 3, which shows that the catalytic activity decreased when increasing the amount of the active phase. Whereas 30CsPMo showed 61% conversion, the sample containing 70 wt% of CsHPA exhibited no more than 8% of conversion. The low activity in this latter case was ascribed to the low dispersion of the active phase, as observed by EDS (cf. Scheme 1), thus resulting in a behaviour comparable to that of a bulk catalyst. With regard to the selectivity to DMA-acetone, a significant decrease was observed when the amount of the active phase was low (30 wt%). In that case, the selectivity to DMA-acetone was no more than 2%, compared to 33% and 30% for the catalysts containing 50 and 70 wt% of the active phase, respectively.

Concerning the observed products, we propose the following reaction mechanism starting from glycerol (Scheme 3). In



Scheme 3 Reaction scheme for the formation of DMA-acetone from glycerol.

the first step, glycerol is dehydrated over the acid catalyst to an enol intermediate (2-propen-1-diol). The latter is not stable and can either further react with dimethylamine to DMAPA or tautomerize to hydroxyacetone. The formation of DMA-acetone can then proceed via amination of hydroxyacetone or by dehydration of DMAPA. As DMAPA was indeed observed during the catalytic tests, we propose that the formation of DMA-acetone involves DMAPA as an intermediate. Furthermore, it is worth mentioning that neither 1,3-bisdimethylamine-2-propanol (BDMAP) nor DMA-propanal was observed. The latter could originate from the amination of acrolein formed by dehydration of glycerol. The corresponding dehydration reaction is well-described over medium to strong acid catalysts.¹²⁻¹⁴ Nevertheless, under the reaction conditions (reaction temperature of 290 °C), all the medium/ strong acid sites should be covered by DMA, whereby they cannot interact with glycerol to enable the formation of acrolein. Consequently, the formation of DMA-propanal was mechanistically made impossible.

In the next step, the optimization of the reaction conditions was performed by computer-assisted design of experiments using a hybrid design (Design-Expert, 11 experiments). Three factors were considered: the reaction temperature, the DMA/GLY ratio and the total reactant flow (contact time). The corresponding values were varied from 260 to 290 °C, 0.5 to 1.5, and 12 to 28 L h⁻¹, respectively. 50CsPMo was selected as the catalyst for this study, due to the fact that it exhibited the highest DMA yield of the series.

Fig. 4 illustrates the influence of the reaction temperature and the DMA/GLY ratio on the conversion of glycerol. At a glance, we can see that the DMA/GLY ratio had a very limited influence on the conversion of glycerol. On the other hand, glycerol conversion clearly increased with the temperature and the reactant flow, reaching up to 70% at 280 °C and 18 L h⁻¹.

The influence of the reaction conditions on the DMAacetone selectivity is shown in Fig. 5. At a reaction temperature of 250 °C and a relatively low reactant flow of 10 L h⁻¹, the selectivity exhibited its maximum at 55%. No absolute optimum in terms of DMA-acetone selectivity was observed for the variation of the DMA/GLY ratio in the range between 0.5 and 1.5.

Following the parameter optimization, we performed a test using the optimal parameter predicted by the model, namely 250 °C, a reactant flow of 10 L h^{-1} and a DMA/GLY



Fig. 4 Glycerol conversion as a function of the reaction temperature and the reactant flow at a constant DMA/GLY ratio of 1.25 (left); glycerol conversion as a function of the reaction temperature and DMA/GLY ratio at a constant reactant flow of 14 L h^{-1} (right).



Fig. 5 DMA-acetone selectivity as a function of the reaction temperature and the reactant flow at a constant DMA/GLY ratio of 1.25 (left); DMA-acetone selectivity as a function of the reaction temperature and DMA/GLY ratio at a constant reactant flow of 14 L h^{-1} (right).



Fig. 6 DMA-acetone yield as a function of the reaction temperature and the reactant flow at a constant DMA/GLY ratio of 1.25 (left); DMA-acetone yield as a function of the reaction temperature and the DMA/GLY ratio at a constant reactant flow of 14 L h^{-1} (right).

ratio equal to 1.5. Using these parameters, a yield of 33% in DMA-acetone was observed (47% conversion and 70% selectivity), which is significantly higher than the value predicted by the model (Fig. 6). These results can be explained by the fact that these parameters are at the boundaries of the value range, where the model is significantly less precise than in the central area.

Conclusions

Various salts of phosphomolybdic acid were used as catalysts in the direct amination of glycerol in the presence of DMA. The use of silica as a support for the cesium salts of phosphomolybdic acid $(Cs_{2.5}H_{0.5}PMo_{12}O_{40})$ significantly increased the amount of acid sites, due to better dispersion of the active phase, thus resulting in an increased conversion of glycerol compared to the parent bulk $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ catalyst. A good distribution was notably obtained for a loading of 50% of the active phase, as shown by IR-Raman and EDS spectroscopy. On the other hand, a higher loading (*i.e.*, 70 wt%) resulted in a bulk-like behavior, whereas a lower loading (*i.e.*, 30 wt%) led to sub-monolayer coverage.

Furthermore, we demonstrated the strong influence of the reaction conditions and notably the reaction temperature on the catalytic performance by employing an experimental design approach. The best performance was obtained over a mesoporous silica-supported $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$ catalyst containing 50 wt% of the active phase, which exhibited a maximum yield of 33% in DMA-acetone.

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